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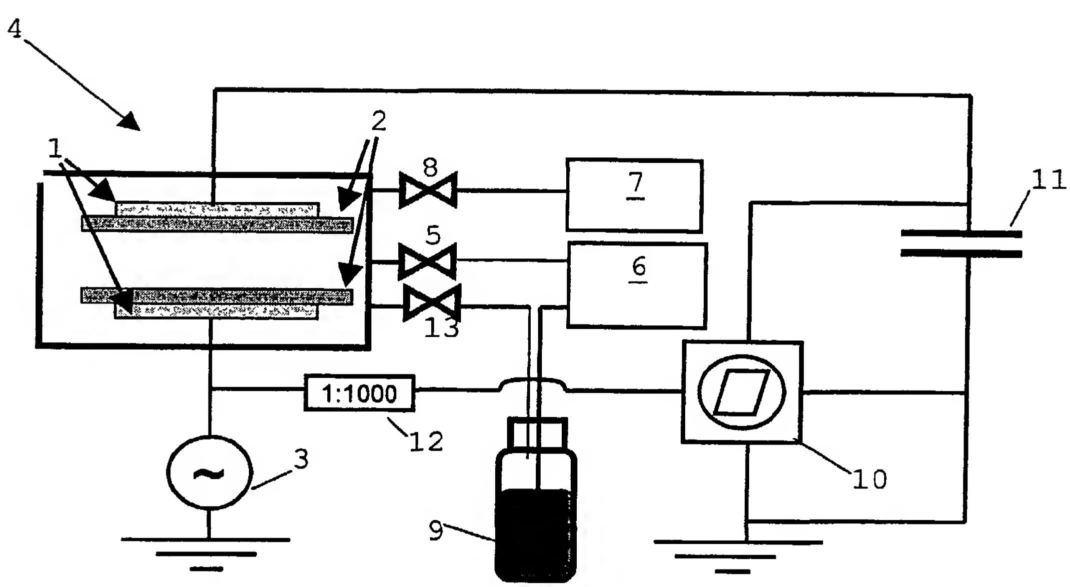
(54) **Title:** METHOD AND APPARATUS FOR GENERATING AND MAINTAINING A PLASMA



(57) **Abstract:** The present invention is related to a method and apparatus for generating and maintaining a plasma by a Dielectric Barrier Discharge technique, in the space between two electrodes, whereby an alternating voltage is applied between said two electrodes, said voltage having such a profile so that one electrode is treated to a lesser degree by said plasma than the other electrode.

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METHOD AND APPARATUS FOR GENERATING AND MAINTAINING A PLASMA

Field of the invention

[0001] The present invention is related to plasma techniques, involving the generation and maintenance of a plasma discharge between two electrodes, for the purpose of cleaning or activation of surfaces, thin film deposition or other.

State of the art

[0002] When chemical compounds are introduced into a plasma discharge, chemically active species are formed such as molecules in excited states, radicals and ions. These species can react with each other, with neutral molecules or with the surface of a substrate. Depending on the nature of the compounds and the process conditions, this may result in cleaning, etching, chemical surface modification (often referred to as activation), deposition of a thin film (often referred to as plasma assisted coating deposition) or the formation of new chemical compounds in the form of gases, liquids or (nano sized) powders.

[0003] The type of plasma discharge wherein at least one electrode is covered by an electrically insulating material, is called "Dielectric Barrier Discharge" (DBD). Dielectric barrier discharges offer interesting

perspectives for cost effective in-line plasma treatments. The configuration of a DBD apparatus generally comprises one or more sets of two electrodes of which at least one is covered with an insulating (dielectric) material. The equipment is especially interesting for innovative surface modification and coating deposition. For this purpose, various organic, inorganic or hybrid (organic/inorganic) precursors can be used. If not gaseous, these precursors are generally applied in the form of vapours of (heated) liquids, aerosols or (nano sized) particles. When such precursors are introduced in a dielectric barrier discharge, deposition of a plasma polymer can occur on the surface of both electrodes.

[0004] In a plasma treatment of any kind, it is normally the purpose to treat the surface of one of the two electrodes, or of a substrate placed in the vicinity of one electrode. However, the treatment of the other electrode is an automatic consequence, even though it is generally undesired. In particular in continuous plasma treatment installations, a high maintenance degree of the machines is required due to fouling of the second electrode. Also, the speed of the plasma treatments is less than satisfactory because of the undesired treatment of the second electrode.

Aims of the invention

[0005] The present invention aims to provide a method and apparatus which allow a DBD plasma treatment to be performed in the space between two electrodes, so that one electrode or a substrate placed in the vicinity of said one electrode is treated to a higher degree than the other electrode.

Summary of the invention

[0006] The present invention is related to a method for generating and maintaining a plasma according to the Dielectric Barrier Discharge (DBD) technique, said method comprising the steps of :

- introducing a sample in the space between two electrodes, a mixed atmosphere being present between said electrodes,
- applying an alternating voltage to said electrodes for generating and maintaining a plasma in the volumetric space between the electrodes, said voltage having a profile as a function of time, defined by a sequence of time periods during which a positive or zero voltage is applied, alternated with time periods during which a negative or zero voltage is applied,

characterized in that said profile is asymmetrical with respect to amplitude and/or time.

[0007] According to the method of the invention, the absolute value of the amplitude of the positive voltage may differ from the absolute value of the amplitude of the subsequent negative voltage. Alternatively, the time period during which a positive voltage is applied may differ from the subsequent time period during which a negative voltage is applied. Finally, the absolute value of the amplitude of the positive voltage as well as the time period during which the positive voltage is applied may be different from respectively the absolute value of the amplitude of the subsequent negative voltage and the subsequent time period during which the negative voltage is applied.

[0008] According to the invention, said plasma is preferably maintained at a pressure in the range between 100Pa and 1MPa. According to a further embodiment, said

plasma is maintained at a pressure in the range between 1000Pa and 1MPa.

[0009] Said mixed atmosphere may comprise one or more of the following components : gases, vapours, aerosols, powders. Said mixed atmosphere may exhibit a compositional gradient.

[0010] Said alternating voltage may have a frequency lying between 10Hz and 50MHz.

[0011] The invention is equally related to an apparatus for generating and maintaining a plasma, preferably in the pressure range between 100Pa and 1MPa, said apparatus comprising a pair of electrodes, a gap being present between said electrodes, and a voltage generator for applying a voltage between said electrodes, said electrodes consisting of an electrically conducting material, wherein one or both electrodes are covered with an electrically insulating material, characterized in that said generator is capable of generating an alternating voltage such as described in appended claim 1.

[0012] In an apparatus of the invention, said electrodes may have the form of planar or curved plates or grids, bars, cylinders, or knife or brush type geometries. One or both of said electrodes may be segmented in different parts of any shape. An apparatus of the invention may comprise a parallel and/or serial combination of one or more of said electrodes. Furthermore, one or both electrodes may be temperature controlled and one or both of the electrodes may be movable.

Short description of the drawings

[0013] Figure 1 shows an example of an applied alternating sinusoidal voltage, asymmetrical in amplitude.

[0014] Figure 2 shows an example of an applied

[0015] Figure 3 shows an example of an applied alternating sinusoidal voltage, asymmetrical in amplitude and time.

[0016] Figures 4 to 6 show additional examples of an applied alternating voltage with a block profile, according to the invention.

[0017] Figure 7 shows a schematic view of an apparatus according to the invention.

[0018] Figure 8 shows a particular voltage profile used in example 2, described in the following paragraph.

Detailed description of the invention

[0019] The present application is related to a method for generating and maintaining a plasma according to a Dielectric Barrier Discharge technique, preferably in the pressure range between 100Pa and 1MPa, said method comprising the steps of :

- introducing a sample in the space between two electrodes, wherein a mixed atmosphere is present between said electrodes,
- applying an alternating voltage to said electrodes for generating and maintaining a plasma in the volumetric space between the electrodes, said voltage having a wave profile defined by a sequence of time periods wherein a positive or zero voltage is applied, alternated with time periods wherein a negative or zero voltage is applied

[0020] According to the invention, the wave profile of the voltage is asymmetrical with respect to amplitude and/or time. This effect can be obtained in three ways :

1. The absolute value of the amplitude of the positive voltage differs from the absolute value of the amplitude of the negative voltage.

2. The time period during which a positive voltage is applied differs from the time period during which a negative voltage is applied.
3. A combination of options 2 and 3

[0021] This can best be illustrated by a number of drawings. Figure 1 shows an alternating voltage wherein during a first period a positive sinusoidal voltage is applied, and during a second period - equal in length to the first period - a negative sinusoidal voltage. The absolute value of the amplitude of the positive voltage is larger than that of the negative voltage.

[0022] Figure 2 equally shows an alternating voltage having different sinusoidal profiles for positive and negative voltages. The time during which the positive voltage is applied is shorter than the time during which a negative voltage is applied. However, the absolute values of the amplitudes are the same.

[0023] Figure 3 shows a profile wherein both the absolute value of the amplitude and the time period are different for the positive and negative voltages. With adequate definition of the actual amplitudes and time frames, this profile equally allows a different energy input during the positive voltage period than during the negative period.

[0024] It is this type of asymmetrical profile which is required in the method of the invention. This can be obtained by applying sinusoidal profiles such as the one shown in figure 1 to 3, or rectangular profiles, such as illustrated in figures 4 to 6. Any other profile shape is possible within the scope of the invention. As seen in figures 4 to 6, it is possible to have a number of off times (zero voltage) between the positive and negative voltage periods. The application of a voltage profile of

while less or little treatment of the second electrode takes place. Examples of specific process conditions are given further in the text.

[0025] The frequency of the alternating voltage profile according to the invention is preferably situated between 10 Hz and 50 MHz.

[0026] Said alternating voltage can be unipolar positive or unipolar negative, i.e. the voltage profile comprises only periods of positive or negative voltage, alternated with periods of zero voltage.

[0027] The mixed atmosphere between the electrodes may consist of any combination of any mixture of gases, vapours, aerosols or powders. In a preferred case, the mixed atmosphere consists of a carrier gas (e.g. helium), mixed with a reactive precursor (e.g. MMA). The mixed atmosphere between the electrodes may exhibit a compositional gradient. Said compositional gradient may be controlled by any combination of following design facilities: gas injection geometry, gas evacuation geometry, electrode geometry, positioning of materials between the electrodes.

[0028] The invention is equally related to a DBD plasma treatment apparatus, equipped with a voltage generator which is able to apply an alternating voltage to two electrodes, said voltage having one of the profiles as described above.

[0029] Figure 7 shows a schematic view of such an apparatus. The apparatus comprises a pump 7 to evacuate the gases, possibly with a control valve 8. An inlet port with possibly a control valve 5 for the gases coming from a gas supply unit 6 and the chemical compounds 13 coming from a supply unit 9. It also comprises at least one set of electrodes 1 which are covered by Al_2O_3 plates 2, which

connected to at least one of the electrodes. The other electrode can be grounded, connected to the power supply 3 or connected to a second power supply. Voltage, charge and current measurements can be performed by means of an oscilloscope 10. For this, one can use respectively a voltage probe 12, a capacitor 11 and a current probe.

[0030] Any known generator capable of delivering a voltage having an asymmetrical profile, can be used. For example the generator provided by ENI, model RPG-50 is a suitable device.

[0031] Such an apparatus further comprises a pair of electrodes, a gap being present between the electrodes, wherein a mixed atmosphere is to be arranged in said gap.

[0032] The electrodes consist of an electrically conducting material and said electrodes can be constructed in any shape but preferentially will take the form of planar or curved plates or grids, bars, cylinders, knife or brush type geometries. One or both of said electrodes consists of an electrically conducting material covered with an electrically insulating material. Furthermore, one or both of said electrodes may be segmented in different parts of any shape. An apparatus of the invention may comprise a parallel and / or serial combination of one or more of said electrodes.

[0033] In an apparatus of the invention, at least one material may be placed between said electrodes. Said material can be a sample requiring a plasma treatment. Said sample can be an organic, inorganic or metallic foil, plate, fibre, wire or powder, a woven or non-woven textile or any combination thereof.

[0034] The plasma treatment conditions at each of the electrode surfaces and at the surfaces of any material placed between the electrodes can differ substantially from

the alternating current voltage applied to these electrodes.

[0035] The plasma treatment conditions can consist of any combination of following operations: etching, cleaning, activation or deposition.

[0036] One or both electrodes in an apparatus of the invention may be temperature controlled. Furthermore, one or both of the electrodes may be movable.

Examples

[0037] A plasma discharge at atmospheric pressure is obtained between two horizontally placed parallel disk-shaped electrodes with a diameter of 150 mm, both covered with an alumina (Al_2O_3) plate of 2 mm thickness. The distance between the covered electrodes is 1 mm. The top electrode is grounded. The bottom electrode is connected to a variable frequency AC power source (ENI, model RPG-50). The frequency of the AC power source is set at 250 kHz. The applied waveform consists of a negative high voltage pulse and a small positive bias pulse. In order to perform tests in a controlled environment, the electrode configuration is mounted in a closed chamber which is evacuated and subsequently filled with the carrier gas before deposition is started.

Helium is used as carrier gas. The flow rate of the carrier gas is controlled by a mass flow controller and set at 15 l/min. Methylmethacrylate (MMA) is used as reactive precursor. It is added to the inert carrier gas in the form of an aerosol. The deposition time was set at 10 min. Coating deposition is observed at the surface of both alumina plates covering the electrodes. However, the coating at the top electrode has a thickness in the order of 0 nm to 150 nm, while the coating on the bottom

[0038] Example 2 : A parallel plate dielectric barrier configuration is used to obtain a plasma discharge at atmospheric pressure. In this particular set-up, the top electrode is covered with an alumina layer of 2 mm. In fact, this electrode is obtained by sputtering Cr on one side of the alumina plate. The top electrode is connected to a high voltage power supply (ENI, model RPG-50). The latter produces a tunable frequency range from 50 kHz to 250 kHz. The bottom electrode is grounded. A glass substrate of 2mm thickness serves as dielectric layer on the bottom electrode. The distance between the electrodes is 1 mm. The voltage profile applied to the electrodes in this case is shown in figure 8.

The gas flow is introduced between the parallel plates via a central gas inlet in the top electrode. The inlet has to be properly isolated from the high voltage electrode. Therefore, it is made out of an alumina tube which is vitrified to the alumina plate. The rest of the gas tubing is made from stainless steel and can be heated. Helium is used as carrier gas. The flow rate of the carrier gas is controlled by a mass flow controller and set at 15 l/min. Hexamethyldisiloxane (HMDSO) is used as reactive precursor. It is added to the inert carrier gas by means of bubbling the carrier gas through a heated reservoir with HMDSO. The bubbler is built up in a simple manner with a low inlet and high outlet connection. The bubbler is made out of stainless steel and is placed in an oil bath on a heating plate. The temperature of the oil bath is controlled by a thermocouple. The maximum temperature of the oil bath is set at 70 °C. The tubing is heated up to 85 °C in order to prevent condensation in the tubing. The deposition time was set at 10 min. Coating deposition is observed at the surface of both alumina plates covering the electrodes.

in the order of 0 nm to 250 nm, while the coating on the bottom electrode has a thickness between 400 nm to 850 nm.

[0039] Example 3 : A parallel plate dielectric barrier configuration is used to obtain a plasma discharge at atmospheric pressure. In this particular set-up, the top electrode is covered with an alumina layer of 2 mm and grounded. In fact, this electrode is obtained by sputtering Cr on one side of the alumina plate. The bottom electrode is connected to a high voltage power supply (ENI, model RPG-50). The latter produces a tunable frequency range from 50 kHz to 250 kHz. A glass substrate of 2 mm thickness, covered with a diamond like carbon coating (DLC) of 1 micrometer thickness, serves as dielectric layer on the bottom electrode. The distance between the electrodes is 1 mm. The DLC coating was applied at the plasma site of the glass plate. The gas flow is introduced between the parallel plates via a central gas inlet in the top electrode. The inlet has to be properly isolated from the high voltage electrode. Therefore, it is made out of an alumina tube which is vitrified to the alumina plate.

The frequency of the AC power source (ENI-RPG50) is set at 250 kHz. The applied waveform consists of a negative high voltage pulse and a small positive bias pulse.

Helium is used as a carrier gas. The flow rate of the carrier gas is controlled by a mass flow controller and set at 20 l/min. No additional chemicals were added to the carrier gas. Etching of the DLC is observed at the surface of the glass plate. After 60 minutes the DLC coating of the bottom electrode is totally etched away.

CLAIMS

1. A method for generating and maintaining a plasma according to the Dielectric Barrier Discharge (DBD) technique, said method comprising the steps of :

- introducing a sample in the space between two electrodes (1), a mixed atmosphere being present between said electrodes,
- applying an alternating voltage to said electrodes for generating and maintaining a plasma in the volumetric space between the electrodes, said voltage having a profile as a function of time, defined by a sequence of time periods during which a positive or zero voltage is applied, alternated with time periods during which a negative or zero voltage is applied,

characterized in that said profile is asymmetrical with respect to amplitude and/or time.

2. The method according to claim 1, wherein the absolute value of the amplitude of the positive voltage differs from the absolute value of the amplitude of the subsequent negative voltage.

3. The method according to claim 1, wherein the time period during which a positive voltage is applied differs from the subsequent time period during which a negative voltage is applied.

4. The method according to claim 1, wherein the absolute value of the amplitude of the positive voltage as well as the time period during which the positive voltage is applied are different from respectively the absolute value of the amplitude of the subsequent negative voltage and the subsequent time period during which the negative voltage is applied.

5. The method according to any one of claims 1 to 4, wherein said plasma is maintained at a pressure in the range between 100Pa and 1MPa.

6. The method according to claim 5, wherein said plasma is maintained at a pressure in the range between 1000Pa and 1MPa.

7. The method according to any one of claims 1 to 6, wherein said mixed atmosphere comprises one or more of the following components : gases, vapours, aerosols, powders.

8. The method according to claim 7, wherein said mixed atmosphere exhibits a compositional gradient.

9. The method according to any one of the preceding claims, wherein said alternating voltage has a frequency lying between 10Hz and 50MHz.

10. An apparatus for generating and maintaining a plasma, preferably in the pressure range between 100Pa and 1MPa, said apparatus comprising a pair of electrodes (1), a gap being present between said electrodes, and a voltage generator (3) for applying a voltage between said electrodes, said electrodes consisting of an electrically conducting material, wherein one or both electrodes are covered with an electrically insulating material (2), characterized in that said generator (3) is capable of generating an alternating voltage such as described in claim 1.

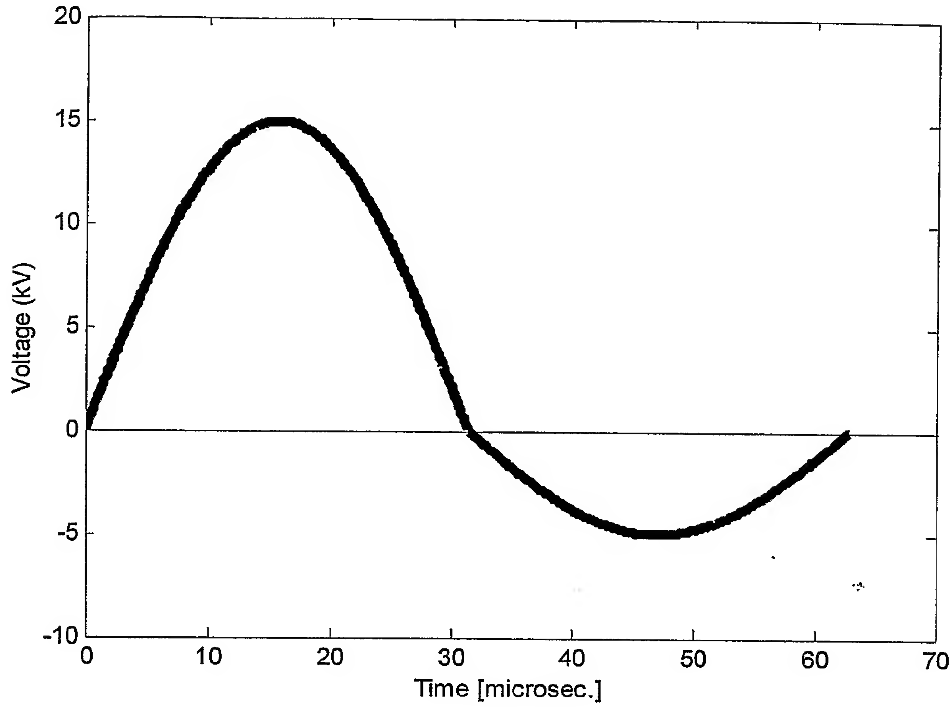
11. The apparatus according to claim 10, wherein said electrodes (1) have the form of planar or curved plates or grids, bars, cylinders, or knife or brush type geometries.

12. The apparatus according to claim 10 or 11 wherein one or both of said electrodes (1) is segmented in different parts of any shape.

13. The apparatus according to any one of claims 10 to 12, comprising a parallel and/or serial combination of one or more of said electrodes (1).

14. The apparatus according to any one of claims 10 to 13, wherein one or both electrodes (1) are temperature controlled.

15. The apparatus according to any one of claims 10 to 14, wherein one or both of the electrodes (1) is movable.



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Time [microsec.]

FIG. 1

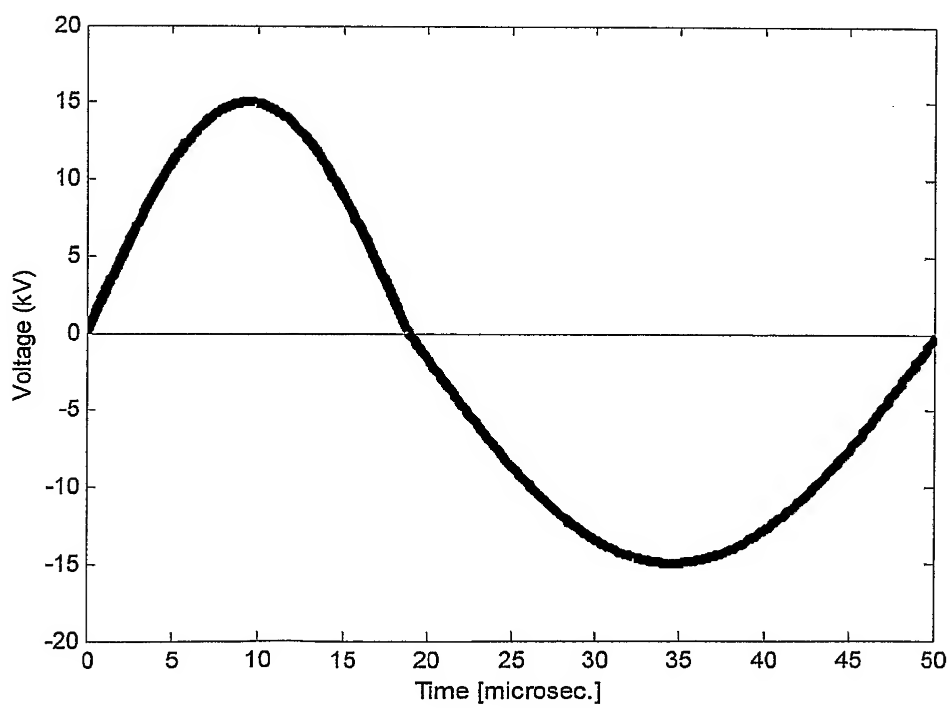

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FIG. 2

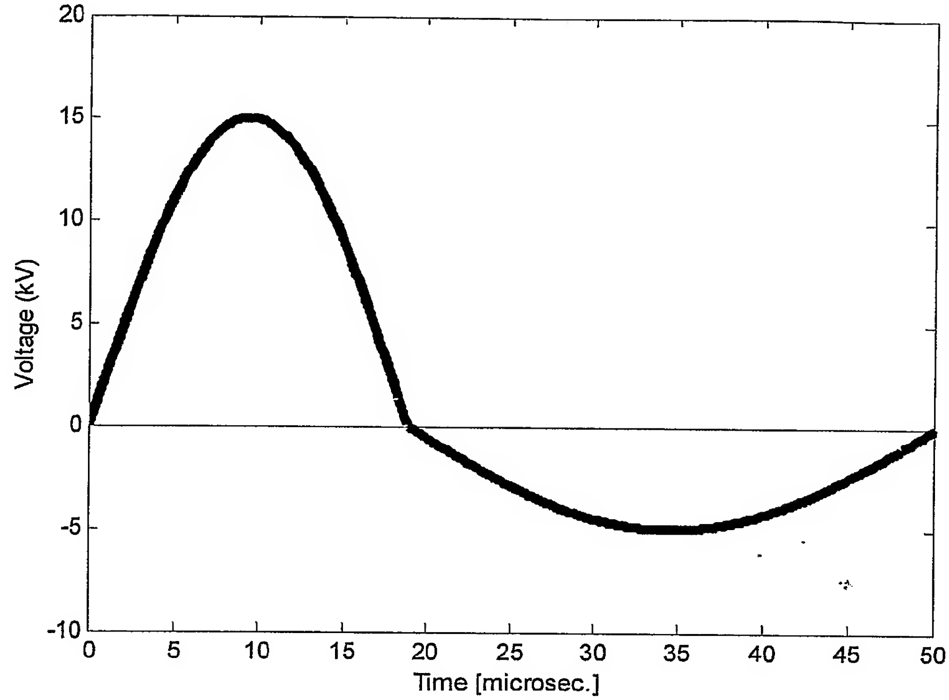
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FIG. 3

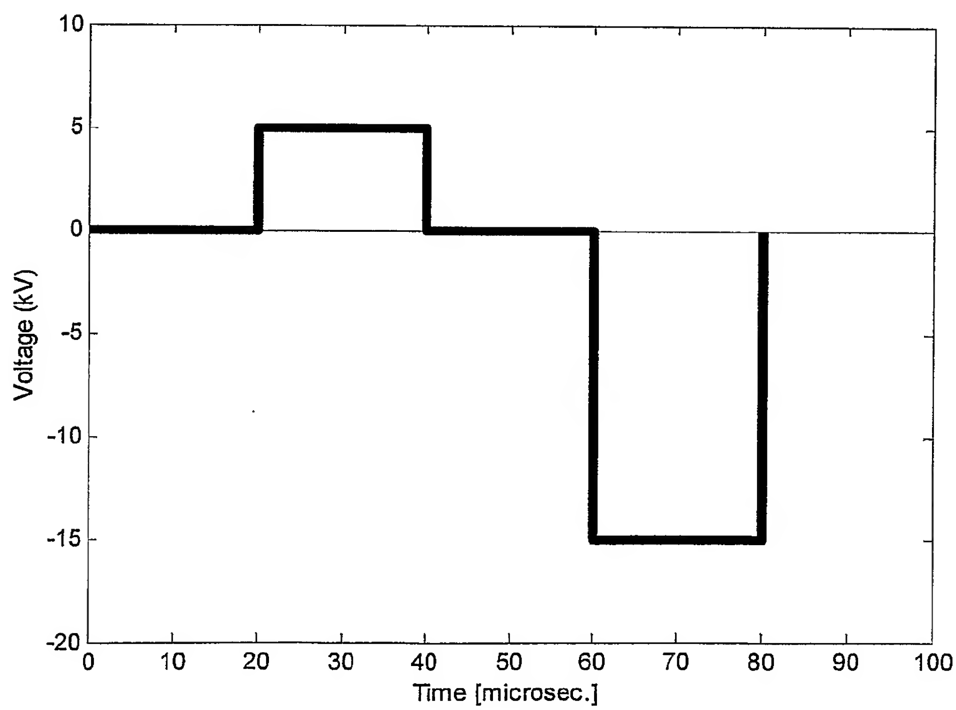
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FIG. 4

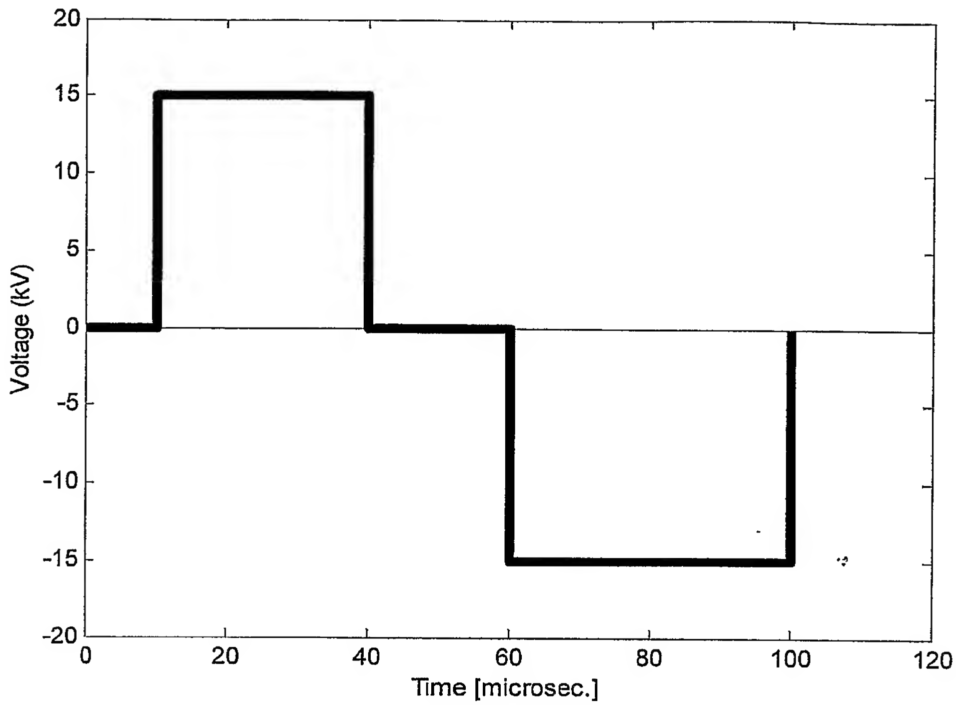
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FIG. 5

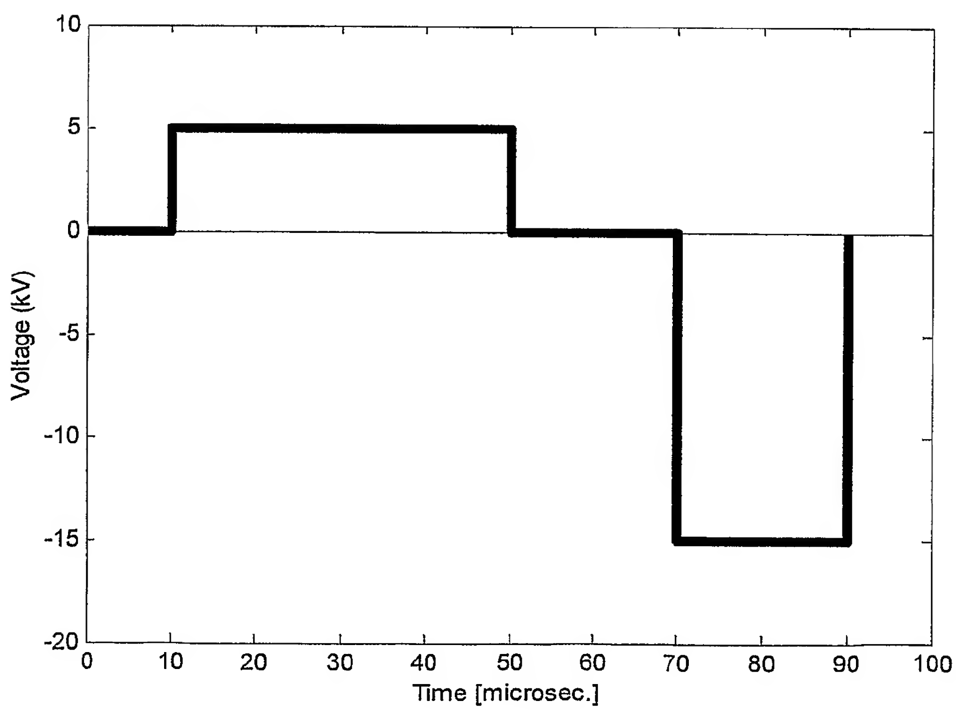
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FIG. 6

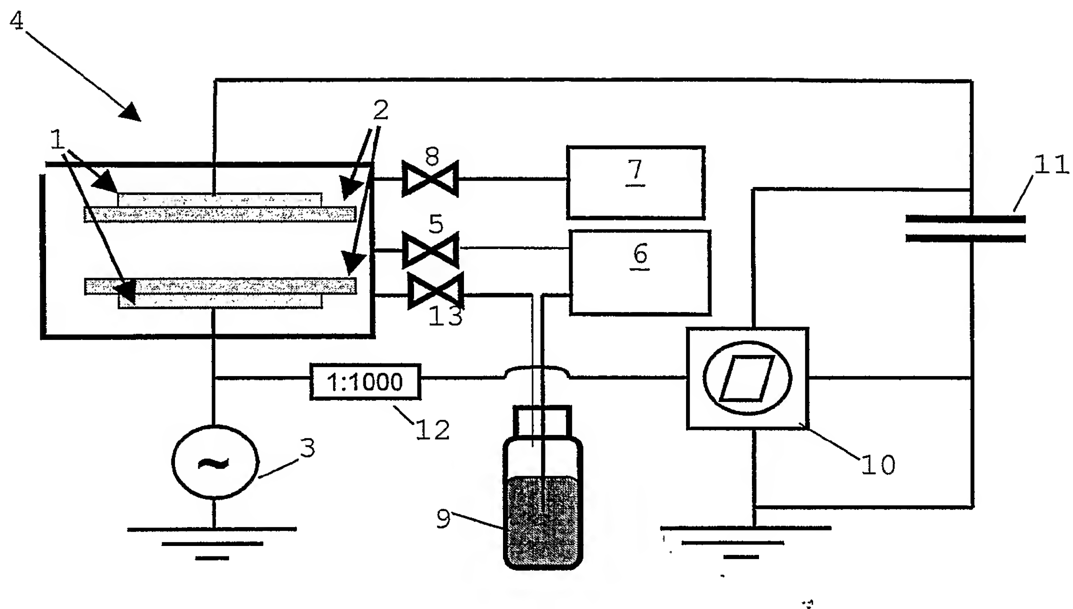
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FIG. 7

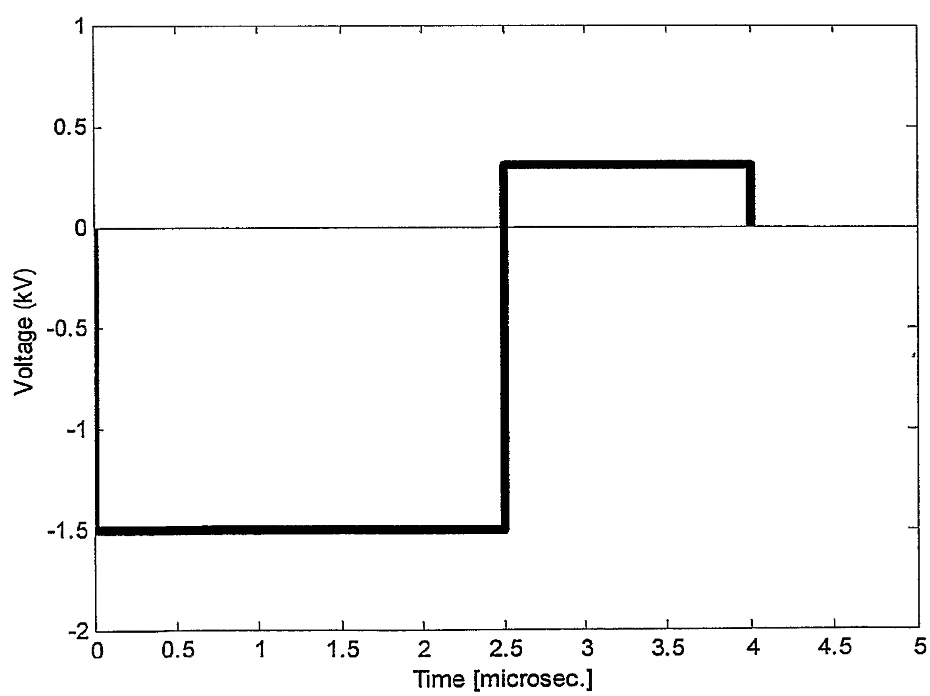
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FIG. 8

INTERNATIONAL SEARCH REPORT

Internatio plication No
PCT/BE 03/00156

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H05H1/24 H01J37/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H05H H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97/13266 A (UNIV TENNESSEE RES CORP) 10 April 1997 (1997-04-10) page 2, paragraph 2 page 5, paragraph 2 page 8, paragraph 3 page 8, last paragraph - page 11, paragraph 1 page 24, paragraph 1 - paragraph ‘0002!	1-7, 9-11,14
Y	claims 4,11,12; figures 1,6,8-a-8b	12,15

Y	WO 01/052302 A (TOKYO ELECTRON LTD ; MITROVIC ANDREJ S (US); JOHNSON WAYNE L (US)) 19 July 2001 (2001-07-19) abstract	12,15

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 December 2003	16/12/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Capostagno, E

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 106 659 A (SPENCE PAUL ET AL) 22 August 2000 (2000-08-22) column 8, line 26 - column 9, line 24 column 14, line 31 - line 34 column 15, line 30 - line 46 column 17, line 1 - line 21 figure 10 -----	1-7, 9-11,14
A	PATENT ABSTRACTS OF JAPAN vol. 0112, no. 73 (C-445), 4 September 1987 (1987-09-04) & JP 62 077479 A (SHIMADZU CORP), 9 April 1987 (1987-04-09) abstract; figures 2,3 -----	1,2,7, 10,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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